PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

A Method for Separating Hydrogen Fluoride in the Production of Fluorine-containing Halogenated Hydrocarbon

We, DAIKIN KOGYO CO., LTD., a corporation organised under the laws of Japan, of Shinhankyu Building, 8 Umeda, Kita-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for separating hydrogen fluoride from a gaseous mixture produced by fluorinating a halogenated hydrocarbon with hydrogen fluoride.

Fluorine-containing hydrocarbons such as dichlorofluoromethane and monochlorodifluoromethane are usually produced from the corresponding chlorinated hydrocarbon by reaction with hydrogen fluoride in the presence of a suitable catalyst; the resulting gas contains unreacted hydrogen fluoride and various fluorinated hydrocarbon byproducts besides the required fluorinated hydrocarbon product, hydrogen chloride and a small amount of the unreacted halogenated hydrocarbon starting material. The separation and purification of the fluorinated product has been performed either by a method which involves cooling the gas mixture to a temperature below the boiling points of the various halogenated hydrocarbon components of the mixture to liquify them, followed, if necessary, by rectification, or by a method which entails removing the hydrogen chloride and hydrogen fluoride by washing with water or alkaline liquor followed by rectification of the halogenated hydrocarbons.

In the former rectification method, when the boiling point of the fluorinated product is close to that of hydrogen chloride or hydrogen fluoride, complicated distillation apparatus is necessary and hence it is difficult in some cases to put this method into practice. In the latter washing method, the halogenated hydrocarbon components of the mixture are insoluble in water but since both hydrogen chloride and hydrogen fluoride are soluble in water, it is necessary to separate both from aqueous solution. For this purpose slaked lime, borax or the like is added to change the hydrogen fluoride to insoluble fluoride leaving hydrochloric acid solution, and it is necesary to regenerate hydrogen fluoride from insoluble fluoride and to concentrate the hydrochloric acid to obtain hydrogen chloride. These procedures are unexpectedly troublesome and require much equipment and accordingly this method is not commercially efficient.

The object of the present invention is to provide a method for separating hydrogen fluoride from such gaseous mixtures which does not have the above drawbacks of these conventional methods.

According to the present invention there is provided a method for separating unreacted hydrogen fluoride from a gaseous mixture produced by fluorinating a halogenated hydrocarbon containing at least one halogen other than fluorine with hydrogen fluoride, the method comprising contacting the gaseous mixture with aqueous sulphuric acid of at least 70 wt. % (based on the total weight of acid+water) concentration to selectively absorb the hydrogen fluoride. The effluent gas may be washed with water so as to recover the hydrogen chloride bromide and/or iodide. The temperature of the sulphuric acid employed is preferably below room temperature, and most preferably below 19° C. The waste sulphuric acid after the above treatment may be used for the manufacture of hydrogen fluoride by reacting it with fluorspar or by heating it to strip off hydrogen fluoride for re-use.

When the sulphuric acid with its absorbed hydrogen fluoride is reacted with fluorspar,

[*Price* 4s. 6d.]

the absorbed hydrogen fluoride together with that newly generated can be recovered by a stripping operation as a pure product useful for fluorination of halogenated hydrocarbons.

In the present method, sulphuric acid absorbs hydrogen fluoride extremely well, namely 1 kg of 98 per cent (by weight) sulphuric acid dissolves 0.75 kg of hydrogen fluoride at a temperature of 20° C. whereas it hardly dissolves the other hydrogen halide or halides. As no water is produced in the fluorination reaction, the above-mentioned conc. sulphuric acid is not as a rule diluted and accordingly it can be used for a long time. Since the boiling point of hydrogen fluoride is about 19° C., the lower the temperature of sulphuric acid employed the better is the solubility of hydrogen fluoride therein. However as the concentration of sulphuric acid gets lower, it tends to dissolve more hydrogen chloride, bromide and iodide and becomes inadequate for fulfilling the object of the invention. Accordingly 70 per cent by weight is the lowest limit of concentration of sulphuric acid useful in the present invention. It is preferable to use an acid of concentration greater than 98 per cent by weight. Sulphuric acid of a concentration of 70 wt. % may also be defined as a mixture of sulphuric anhydride and water containing 57 wt. % of SO_3.

The effectiveness of H_2SO_4 in absorbing HF according to the invention is illustrated in the accompanying drawings in which:

Figure 1 is a diagram showing the liquid-gas equilibrium of hydrogen fluoride at room temperature between a gaseous mixture and conc. sulphuric acid, the composition of the gaseous mixture being monochlorodifluoromethane

$$\frac{\text{HF}}{\text{HCl}} = \frac{1}{2} \text{ (mol ratio)},$$

the concentration of hydrogen fluoride is expressed in weight percent. It will be seen that the HF is preferentially absorbed into the acid;

Figure 2 shows the result of an experiment in which conc. sulphuric acid at room temperature is sprayed from the top of a tower countercurrent to an ascending mixture of HF gas with a gaseous mixture of the composition given for Figure 1. The ordinate in this figure indicates the concentration of hydrogen fluoride (percentage by weight) in the solution obtained when the gas issuing from the top of the tower is introduced into water and made into 33 per cent (by weight) hydrochloric acid.

The following Example of the method according to the invention is given by way of illustration only.

EXAMPLE

A gaseous mixture generated in the production of monochlorodifluoromethane from chloroform and hydrogen fluoride was introduced into the bottm of a tower from the top of which 98 per cent (by weight) conc. sulphuric acid at room temperature was sprayed. The gaseous mixture ascended the tower and the gas issuing from the top of the tower was passed through an entrainment separator and then washed with water to dissolve hydrogen chloride. Subsequently the gas was cooled to a temperature of 6° C. at a pressure of 6 kg/cm², and the main product $CHClF_2$, various byproduct halogenated hydrocarbons such as dichloromonofluoromethane and trifluoromethane and unreacted chloroform were separated by liquification. The conc. sulphuric acid drawn from the bottom of the tower was heated to a temperature of 120° C. to remove absorbed HF and recycled to the top of the above-mentioned tower. The result of operation is as follows:

Velocity of gas introduced at the bottom	4.5 kgmol/hr.
*Composition of gas introduced at the bottom	$CHClF_2$ 52.2% by weight HCl 44.0% by weight HF 3.8% by weight
Amount of 98% conc. sulphuric acid passed from the top	150 kg/hr.
Amount of hydrogen fluoride absorbed	8.2 kg/hr.
Hydrogen fluoride recovered by stripping	7.8 kg/hr.
Amount of hydrogen fluoride in the purified gas	0.09% by weight

*The total amount of dichloromonofluoromethane, trifluoromethane and other components is less than 0.1 wt. %.

The present invention can also be applied effectively, for example, in the purification of the exhaust gas obtained when trichloromonofluoromethane and/or dichlorodifluoromethane is produced from carbon tetrachloride and hydrogen fluoride, and when trichlorotrifluoroethane (usually accompanied by dichlorotetrafluoroethane and/or monochloro-

pentafluoroethane) is produced from tetrachloroethylene, chlorine and hydrogen fluoride.

WHAT WE CLAIM IS:—

1. A method for separating unreacted hydrogen fluoride from a gaseous mixture produced by fluorinating a halogenated hydrocarbon containing at least one halogen other than fluorine with hydrogen fluoride, the method comprising contacting the gaseous mixture with aqueous sulphuric acid of at least 70 wt. % concentration to selectively absorb the hydrogen fluoride.

2. A method according to Claim 1, wherein the temperature of the sulphuric acid is below room temperature.

3. A method according to Claim 2, wherein the temperature of the sulphuric acid is below 19° C.

4. A method according to any of Claims 1 to 3, wherein the sulphuric acid is sprayed countercurrent to an ascending stream of the gaseous mixture.

5. A method according to any of Claims 1 to 4 for the purification of a gaseous mixture obtained by the fluorination with hydrogen fluoride of a chlorine-containing halogenated hydrocarbon, the method comprising contacting the gaseous mixture with aqueous sulphuric acid of at least 70 wt. % concentration to selectively absorb the unreacted hydrogen fluoride and thereafter washing the remaining gases with water to remove hydrogen chloride.

6. A method according to any of Claims 1 to 6, wherein the sulphuric acid contacted with the gaseous mixture is reacted with fluorspar to free the absorbed hydrogen fluoride and to generate fresh hydrogen fluoride.

7. A method according to any of Claims 1 to 5, wherein the sulphuric acid contacted with the gaseous mixture is heated to strip off the absorbed hydrogen fluoride.

8. A method according to Claim 6 or 7, wherein the recovered sulphuric acid is recycled for re-use.

9. A method according to Claim 6 or 7 or to Claims 6 to 8 wherein the recovered hydrogen fluoride is recycled for re-use in the fluorination of halogenated hydrocarbon starting material.

10. A method according to any of Claims 1 to 9, wherein the halogenated hydrocarbon starting material is a saturated aliphatic halogenated hydrocarbon.

11. A method according to Claim 1 substantially as hereinbefore described.

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1 SHEET This drawing is a reproduction of the Original on a reduced scale

FIG. 1

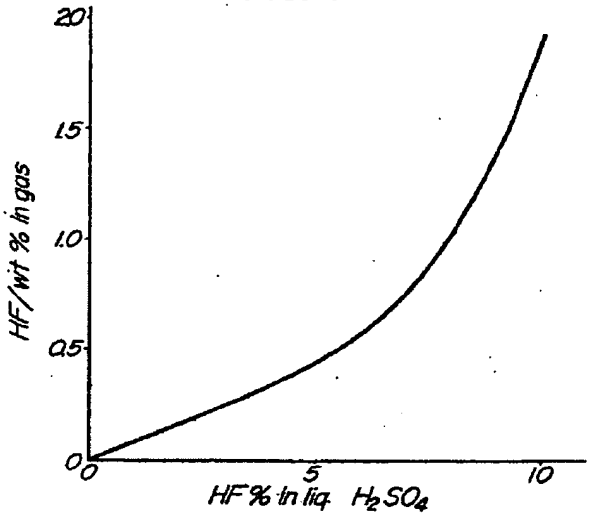

FIG. 2